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ties arranged in order of intensity from white to intense dark red is one of graduated differences in amount of a single pigment rather than in qualitatively different pigments. A definite alternative analysis can, however, be made even for these semi-quantitative characters by growing successive generations of segregating progenies until the progenies have been freed of segregation products other than those which it is desired to analyze. Furthermore, the establishment of constant derivative races and the subsequent study of intercrosses among them has been found to result in simplification of the difficulties of analysis. Both of these methods evidently depend upon stabilizing the residual genotype, which is a prime desideratum in the accurate analysis of semi-quantitative characters. The fact that such simplification of segregation can be accomplished and that semi-quantitative characters may then be subjected to analysis according to the qualitative mode of procedure argues not only for the adequacy of Mendelian principles in these cases, but for the identity in principle of qualitative and quantitative characters.

The experimental data cited above were obtained from cultures made possible by a portion of the Adams' Fund allotted to the Department of Botany by the Department of Agriculture of the University of California. The detailed account of this series of studies will appear in a forthcoming number of Vol. 5 of the University of California Publications in Botany under the title, Studies of inheritance in *Nicotiana Tabacum*, I. A report on the results of crossing certain varieties.

¹ Comes, O.: "Monographie du genre *Nicotiana* comprenant le classement botanique des tabacs industriels," *Atti. R. Inst. Incoraggiamento, Napoli* (Ser. 5), **1**, 1899.

"Della Razze dei Tabacchi Filogenesi, Qualita ed Uso," *Ibid.*, **57**, 1905.

² Anastasia, G. E.: "Le varietà Tipiche della *Nicotiana Tabacum* L. Scafati, 1906.

³ Setchell, W. A.: "Studies in *Nicotiana*, I," *Univ. Calif. Publ. Botany*, **5**, 1912 (1-88).

⁴ Allard, H. A., "Some studies in blossom color inheritance in tobacco, with special reference to *N. sylvestris* and *N. Tabacum*," *Amer. Naturalist*, **53**, 1919 (79-84).

THE CORRELATION OF COMPOUND FORMATION, IONIZATION AND SOLUBILITY IN SOLUTIONS. OUTLINE OF A MODIFIED IONIZATION THEORY

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Introduction.—The anomaly of strong electrolytes has been a notoriously weak point in the ionization hypothesis ever since its inception. In fact, satisfactory agreement with the Ostwald dilution law (which follows from the application of the law of mass action to the ionization equilibrium $RX \rightleftharpoons R^+ + X^-$) has been definitely established only for two restricted types of electrolytes (weak acids and bases) in a single solvent (water) through a limited concentration range (dilutions greater than $N/16$).

Numerous attempts towards reconciliation having failed, the tendency is now wide-spread either to deny the applicability of the law of mass action to the ionization of strong electrolytes or to modify the ionization equation itself.

Complete ionization of strong electrolytes, with an electrostatic equilibrium between "free" and "bound" ions, has recently been urged by Milner, Ghosh and others. The existence of inter-ionic attractive forces and the necessity for recognizing their effect in any accurate ionization formula cannot be questioned, yet there are several points of difficulty which the Milner-Ghosh conception still leaves unexplained. Among these may be mentioned the lack of a definite gap between strong and weak electrolytes and the fact that the heat of ionization (as ordinarily defined) does not agree at all with the work required for the separation of the charged radicals. It is quite possible, indeed, that the concordance obtained by Ghosh between experimental and calculated "ionization" values may ultimately prove to be due rather to convenience of constants than to the fundamental validity of the equations developed. Full discussion of these points must be reserved for a future article. A still more serious objection, however (which applies also to the original hypothesis of Arrhenius), is the neglect of the rôle of the solvent in ionization.

The essential equivalence of solvent and solute in ionization equilibria has been elaborated upon in a previous paper.¹ We take two liquids; for example, water and (liquefied) hydrogen chloride. Both are highly associated, both have high dielectric constants, both possess practically zero conductivity when perfectly pure. We mix them and obtain a solution with very high conductivity, which we ascribe to the dissociation of the hydrogen chloride into its constituent ions. Is there really any reason why the conductance should be referred entirely to hydrogen chloride and not at all to water? The *active* part played by the solvent in ionization is unconsciously recognized by our admission that ions are "hydrated" in aqueous solution, since (for example) a "monohydrated chlorine ion" ($\text{Cl}, \text{H}_2\text{O}$)⁻ might just as conceivably deserve the alternative title of a "solvated hydroxyl ion" (HCl, OH)⁻. A scheme according to which water is the only "ionizing" substance in all aqueous solutions would, in point of fact, be quite as logical (and certainly as simple) as the scheme at present employed, which relegates water to the inferior rôles of "dead space" and "envelopes." Much more satisfactory than either, however, would be a theory taking both components of a conducting solution equally into account.

Considerable experimental work, upon which such a theory may be based, has been performed by the author and his collaborators² during the past seven years. The main results and the conclusions to which they lead are summarized below.

At the beginning of the work, it was felt that the most familiar case of

aqueous solutions would be better postponed, since the complexity of the equilibria here undoubtedly confuses the issue. Generalizations for non-aqueous solutions were accordingly first sought, with the idea of testing their applicability to aqueous solutions (where data for the purpose are plentiful) at as early a stage as possible.

Ionization and Ideality.—The most significant characteristic of all conducting solutions is that they are non-ideal. Two non-associated substances, chemically inert one towards the other, never give a conducting solution on admixture. Ionization is consequently always accompanied by interactions between the "solvent" and "solute." How to connect the extent of these interactions with the character of the two components was the first problem to be attacked.

Now the character of the two components AB and CD in a conducting solution, as related to ionization, may obviously be varied by varying the "ionization tendency" (or "electro-affinity") of the constituent radicals A , B , C and D . A definite experimental criterion of such variations is afforded by electromotive force measurements (for inorganic radicals) and by comparison of ionization constants (for organic radicals). The results obtained in these fields have therefore been utilized to investigate the influence of the character of the constituent radicals upon interactions between the components in solutions of widely different types.

Compound Formation and Electroaffinity.—The first type of system studied contained but one variable radical. Dimethylpyrone (a weak base in aqueous solution) was chosen as one component, acids of widely divergent character were taken as the second, and the extent and stability of compound formation on admixture were established for each particular case by examination of the freezing-point depression curves. The only variable factor here was the electroaffinity of the radical X of the acid component HX . The experimental results demonstrated that compound formation in the system regularly increased as X became more negative.

Systems with more than one variable radical were next investigated. For example, aldehydes of widely divergent character were substituted for dimethylpyrone and tested against different acids. It was found that compound formation was uniformly more extensive the more electro-positive the radical R of the aldehyde $R.CHO$ and the more electro-negative the radical X of the acid HX . Similarly with systems of the type ester-acid the extent of compound formation increased regularly as the radicals R and R^1 of the ester $R.COOR^1$ were made more electro-positive, or as the radical X of the acid HX was made more electro-negative. With systems of the type acid-acid, finally, it was shown that the weaker acid HX functioned as a base with regard to the stronger acid HY , the stability of the resultant salt being greater the greater the difference in the electroaffinity of the radicals X and Y . Incidentally no

fewer than 96 new organic compounds have been isolated in the course of this work.

Compound formation in binary organic mixtures is therefore fundamentally dependent upon diversity in character (i. e., differences in positive or negative natures of the constituent groups) of the two components.

Compound Formation and Ionization.—Before proceeding further, it was necessary to confirm a point which the above results had indicated as highly probable—namely, that the order of electroaffinity of different radicals in these organic mixtures was substantially the same as in aqueous solutions. This was satisfactorily established by careful conductivity determinations upon various systems of the types examined above. In a fixed ketone or ester, for example, different acids HX were found to give more highly conducting solutions the more electronegative the radical X . In a fixed acid HX , conversely, different ketones $R.CO.R^1$ or esters $R.COOR^1$ gave solutions of better conductivity the more electropositive the radicals R and R^1 . Different acids HY in a fixed acid HX , finally, gave more highly conducting solutions the greater the difference in the electroaffinity of the radicals X and Y .

An important generalization may therefore be deduced: in a conducting solution, *compound formation* between the components and *ionization* proceed in parallel. Where compound formation is very slight, ionization is inappreciable; as compound formation increases in extent, ionization becomes evident; where compound formation is very marked, ionization is extensive.

The validity of this generalization for aqueous solutions may now be examined. Acids and bases obviously furnish a stringent test, since ionization here varies very considerably. Examination of the available data shows that *strong* acids invariably give stable hydrates, while among the myriads of *weak* acids listed in Beilstein not a single example of hydrate formation is indicated. Quantitative confirmation of the parallelism between hydrate formation and ionization for acids in aqueous solution was obtained from freezing-point depression determinations with a series of acids of gradually increasing strength. With bases the data, though not so extensive, showed similar agreement.

A Modified Ionization Theory.—On the basis of the above results, a modification of the current ionization theory has been proposed, under the assumption that "ionization is preceded by combination between solvent and solute and is, indeed, a consequence of such combination." According to this view, ionization in solutions is due not to solute alone nor to solvent alone, but to combination between the two to form unstable complexes. The various factors affecting the formation and stability of such complexes have been critically discussed elsewhere.³ It has been shown that, while in simple molecules the two radicals are in general attracted to each other so strongly that no dissociation is observable, yet

in complex "addition compounds" the attractive forces between the radicals are so diminished that disintegration of the complex into oppositely charged ions may readily occur. *Union with another molecule promotes ionization.*

The theoretical arguments in favor of this assumption and the experimental evidence in its support cannot be presented in detail here. The immediate consequence of the modified ionization theory, as connected with the anomaly of strong electrolytes, may however be indicated.

Instead of a simple equilibrium such as $KCl \rightleftharpoons K^+ + Cl^-$ for a univalent electrolyte in aqueous solution, we now have to consider a complicated series of equilibria between many different molecular and ionic types, such as $(KCl)_x$; $(KCl)_x$, $(H_2O)_y$; $[(KCl)_x, Cl]^-$; $[(H_2O)_y, Cl]^-$, etc. To some of these equilibria the law of mass action alone may apply, to others the Milner-Ghosh conception of electrostatic equilibrium may need to be superadded. Little wonder, therefore, that the problem has baffled all attempts at explanation under the hypothesis $RX \rightleftharpoons R^+ + X^-$. If we persist in postulating the reaction as inconceivably simple, we can hardly expect to make progress, even in the field of dilute solutions, where many of the equilibria may be neglected.

It might seem that the complexity in the equilibria necessarily introduced by the consideration of so many molecular types could, after all, only make the problem still more intricate and elusive. The first effect, nevertheless, is in the opposite direction. Many subsidiary assumptions which have been attached to our theory of solutions in order to conceal the failure of the simple equation $RX \rightleftharpoons R^+ + X^-$ may now be shown to be unnecessary. For example, the hypothesis of the "catalytic activity of the undissociated molecule," which purports to explain why the speed of reactions such as ester catalysis is not exactly proportional to hydrogen ion concentration, may be discarded in favor of a view which recognizes several types of "hydrogen ion" (e. g., H^+ , $[H(H_2O)]^+$, $[H(R.COOR')]^+$) each possessing a different catalytic activity. In the same way abnormal results in electromotive force measurements, which have been interpreted as demonstrating a variable activity of the hydrogen ion with concentration, may now be alternatively referred to variations in the ratios of the different types of "hydrogen ion" with concentration. There is no more reason, for instance, why the ion $[H(H_2O)]^+$ should show the same potential difference as the ion H^+ with respect to gaseous hydrogen than there is for the ion $[Cu(NH_3)_y]^{++}$ to exhibit the same potential difference as the ion Cu^{++} with respect to metallic copper. The extension of the theory of complex ions to simple aqueous solutions is evidently one of the first steps to be taken in the further development of the views here presented. Detailed discussion must be postponed to a later article.

Salts in Aqueous Solution.—The correlation of compound formation and ionization in this important field offers difficulties. Nearly all uni-

univalent salts are practically equally dissociated in aqueous solution, yet hydration values so far as we can judge from present data are widely divergent. It is a very striking fact, however, that with mercuric salts (the one series in which ionization varies considerably) *all* highly ionized salts yield hydrates (e. g., $Hg(NO_3)_2 \cdot 8H_2O$; $Hg(ClO_4)_2 \cdot 6H_2O$; $HgF_2 \cdot 2H_2O$) while *all* slightly ionized are non-hydrated.

It appeared that the problem might be taken up most profitably in two stages—by the examination of systems of the type $RX-HX$ (acid salts) and of the type $RX-ROH$ (basic salts). By comparison of the results in these fields with those already obtained for systems of the types: $HX-H_2O$ and $ROH-H_2O$ it was hoped that generalizations for the more complex type $RX-H_2O$ might be successfully formulated. The results obtained from a detailed investigation of two series of acid salts (formates and sulfates) have justified this procedure.

Acid Salts.—Compound formation in the system acid-salt is found to be directly dependent upon differences in electroaffinity, as before. With salts of highly electropositive metals (e. g., K , Na) extensive compound formation is obtained. As the metal approaches hydrogen in the electromotive series, compound formation decreases rapidly (with Ba , Ca , Mg) and finally becomes negligible (with Ni , Fe , Cu). With highly electronegative metals, however (Hg , Ag), compound formation once more becomes appreciable. Ionization again proceeds in parallel with compound formation, the best conducting solutions in pure formic or sulfuric acid being given by the salts of K and Na .

Solubility.—A new and very significant relationship which appears in these systems is that of solubility, which also parallels compound formation. The sulfates of K and Na are exceedingly soluble in pure H_2SO_4 , those of Ba , Ca and Mg are decreasingly soluble, those of Ni , Fe , Cu practically insoluble. With electronegative metals the solubility again becomes appreciable (with Hg) and finally extensive (with Ag). The solubilities of the formates in formic acid follow exactly the same course.

That the rule is valid also in aqueous solutions may be demonstrated by applying it to systems of the type $ROH-HOH$. The hydroxides of the alkali metals are very soluble in water, those of the alkaline earths decreasingly soluble, those of Ni , Fe , Cu practically insoluble. Silver again shows an increase, limited however by precipitation of the more stable oxide.

In systems of the type $RX-HOH$, finally, the same rules hold if R is not very different in character from H , or if X is not very different in character from OH . Thus the salts of weak bases (e. g., ferric salts) or of weak acids (e. g., fluorides) show regular gradations of solubility in water, which substantially follow the generalizations given above. For salts of a strong acid with a strong base, however, where R and X both differ widely in

character from H and OH , no such simple behavior is to be expected, nor is it found. Rules for such systems have still to be discovered.

The reason for the above dependence of solubility upon compound formation becomes evident when we examine the freezing-point depression curve of a system such as $Li_2SO_4-H_2SO_4$. The absolute freezing-point of the salt is so high that, unless compound formation took place, solubility in the acid at ordinary temperatures would, according to the Schröder-Le Chatelier equation,⁴ necessarily be negligible. The removal of simple solute molecules by combination with solvent, however, results in an increased solubility, and the extent of such increase depends, naturally, upon the extent of compound formation. The further development of this topic and the presentation of quantitative results will be given in forthcoming articles in the *Journal of the American Chemical Society*.

* Contribution No. 350.

¹ Kendall and Booge, *J. Amer. Chem. Soc.*, **39**, 1917 (2323).

² Carpenter, Ph.D. *Dissertation*, Chicago, 1915; Gibbons, *J. Amer. Chem. Soc.*, **37**, 1915 (149); Booge, Ph.D. *Dissertation*, Columbia, 1916; Gross, Ph.D. *Dissertation*, Columbia, 1919; Landon, Ph.D. *Dissertation*, Columbia, 1920; Adler, Ph.D. *Dissertation*, Columbia, 1920; Davidson, Ph.D. *Dissertation*, Columbia, 1920.

³ Kendall and Booge, *loc. cit.*; Gross, *loc. cit.*

⁴ Roozeboom, *Heterogene Gleichgewichte*, **2**, 1904 (270-84).

THE PELTER EFFECT

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When a current of electricity goes from metal α , in which the free-electron fraction of the conductivity is $(k_f \div k)_\alpha$, to the metal β , in which the corresponding fraction is $(k_f \div k)_\beta$, ionization or reassociation must take place at the junction, according as $(k_f \div k)_\beta$ is greater or less than $(k_f \div k)_\alpha$. The resulting change of condition is the same whether we assume the ionization or reassociation to take place after or before the crossing of the interface between α and β . We shall use each of these hypotheses in turn, beginning with the first.

The gain of energy, and so the heat energy absorbed, by the unit quantity of electricity, 10 coulombs, in the form of electrons, in crossing the boundary from α to β is

$$\Pi = \left(\frac{k_f}{k} \right)_\alpha \left(P_\beta - P_\alpha \right)_f + \left(\frac{k_a}{k} \right)_\alpha \left(P_\beta - P_\alpha \right)_a + \left(P_\beta - P_\alpha \right) + \left[\left(\frac{k_f}{k} \right)_\beta - \left(\frac{k_f}{k} \right)_\alpha \right] \lambda_\beta, \quad (1)$$

where $(P_\beta - P_\alpha)_f$ means the P_f of β minus the P of α , etc., the nomenclature according in general with that of my preceding papers.